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MECHANISM OF GROWTH OF SILICON NITRIDE CRYSTALS IN COMBUSTION OF FERROSILICON IN NITROGEN

L. N. Chukhlomina¹ and Yu. M. Maksimov¹

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The process of nitride formation in burning of iron – silicon melt in gaseous nitrogen was investigated. It was found that silicon nitride is synthesized at temperatures (2100°C) which are much higher than the temperature of appearance of the liquid phase (1206°C). Silicon is in the liquid state during synthesis in the form of an iron – silicon melt and a gaseous melt. The electron-microscopic studies showed that silicon nitride crystals grow according to two mechanisms: vapor – liquid – crystal and crystallization from iron – silicon melt. The ratio of the contributions of these mechanisms to structural formation of silicon nitride is determined by the conditions of synthesis.

Ceramic materials based on silicon nitride have high resistance to oxidation and corrosion, thermal stability, hardness, and wear resistance and are considered as the most promising materials in construction ceramics [1]. Silicon nitride powder is usually obtained by reacting silicon with gaseous nitrogen. In [2, 3], this reaction was also conducted by burning the silicon powder in nitrogen in the combustion mode (method of self-propagating high-temperature synthesis — SHS). They showed that Si_3N_4 crystals grow according to the vapor – liquid – crystal mechanism in the combustion wave. Synthesis of silicon nitride in combustion of ferrosilicon alloy in gaseous nitrogen has also been investigated (RF Patent No. 2257338) [4]. It was shown that the product of combustion of ferrosilicon in nitrogen is a composite of silicon and iron nitride. After acid concentration in hydrochloric acid solutions, silicon nitride powder with a 0.05% residual iron content² is obtained. Use of alloys of silicon and iron as feedstock solves two problems: reducing the cost of silicon nitride and utilizing powdered industrial ferrosilicon wastes which is important for ferroalloy plants.

We report the results of a study of the mechanism of growth of silicon nitride crystals in combustion of Fe – Si melt in nitrogen.

Powdered ferrosilicon wastes PUD-75 — polydisperse powder with a particle size of less than 160 μm and 82.0% silicon content — were used as the feedstock. X-ray phase analysis showed that the alloy was a two-phase material consisting of silicon and high-temperature lebeauite FeSi_2 .

The ferrosilicon powder was poured into cylindrical metal gauze tubes 38–60 mm in diameter. The samples were burned in a constant-pressure unit in nitrogen atmosphere. The nitrogen pressure varied from 1 to 10 MPa. The samples were ignited from a powdered incendiary mixture with a tungsten coil through which an electric current was passed. After passage of the combustion front, the sample was held in the nitrogen atmosphere until it had totally cooled, the pressure was then released, and the product was removed from the unit for further investigation. The samples were quenched by abruptly releasing the nitrogen pressure and quickly filling the constant-pressure unit with argon.

The x-ray phase analysis was conducted on a DRON-2 diffractometer using Co radiation. The electron microscopic studies were conducted with a JEM-100CXII electron microscope with an ASID-4D scanning attachment (JEOL, Japan). The chemical composition of the combustion products was investigated by micro-x-ray spectral analysis on a Camebax – Microbeam unit. The combustion temperature was measured with a tungsten – rhenium thermocouple (VR5 – VR20) 100 μm in diameter, inserted in the sample to a depth of 15 mm.

The products of combustion of ferrosilicon in nitrogen had pronounced shape anisotropy (Fig. 1) and are whisker, acicular, and lamellar crystals. As a result of the microx-ray spectral analysis, it was found that these were silicon nitride crystals. Iron (approximately 10%) in the form of spherical, partially fused particles was uniformly distributed in the combustion product.

According to the published data, whiskers can grow from the liquid and gas phases [5]. Formation of silicon nitride ac-

¹ Tomsk Science Center, Siberian Branch, Russian Academy of Sciences, Tomsk, Russia.

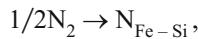
² Hear and below — the weight content.

According to a solid-phase mechanism during SHS is not very probable, since the maximum combustion temperature (measured with a thermocouple) is 2100°C. As a consequence, silicon nitride is synthesized at temperatures which are much higher than the temperature of appearance of the liquid phase (1206°C). Silicon will either be in the liquid state in the form of a ferrosilicon melt or in the gas state during synthesis.

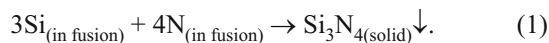
The solubility of nitrogen in liquid silicon is low and is 0.01% at 1450°C. The solubility of nitrogen in liquid iron is slightly higher than in silicon, but at 1760°C does not exceed 0.044%. According to the data in [6], silicon reduces the solubility of nitrogen in liquid iron, but increases its activity coefficient. Since SHS takes place at high nitrogen pressure P_{N_2} , with an increase in the pressure above the liquid melt according to Sieverts law

$$[N] = f\left(\sqrt{P_{N_2}}\right)$$

the equilibrium nitrogen content in the melt also increases. The gaseous nitrogen dissolved in the melt



reacts with the silicon and silicon nitride is formed according to the reaction:



A system is formed during combustion in which a diffusibly soluble compound is in equilibrium with a saturated solution of this compound in the iron – silicon melt. In conditions of equilibrium, the product of the activities of nitrogen and silicon in degrees equal to their stoichiometric coefficients is the solubility product $SP_{Si_3N_4}$ of silicon nitride in iron. The solubility product of Si_3N_4 in iron silicide is low and is 4.5×10^{-10} at 1000°C, while the equilibrium nitrogen content is $[N] = 0.0019\%$. It follows that insignificant concentrations of dissolved nitrogen are sufficient for formation of silicon nitride in liquid ferrosilicon. The equilibrium of the examined system characterized by reaction (2) is shifted toward formation of the reaction product (Si_3N_4 in the solid phase), which is constantly removed from the system. The composition of the ferrosilicon melt changes constantly during synthesis toward an increase in the iron content. Gradual enrichment of the ferrosilicon melt with iron accelerates formation of silicon nitride in the melt due to the greater solubility of nitrogen in iron than in Fe – Si melts.

The study of the microstructure of hardened samples of nitrated ferrosilicon showed that the ferrosilicon melt drop has a developed surface on which many nuclei and growing silicon nitride crystals are visible (Fig. 2).

The growing crystals affect the boundary liquid layers so that they acquire a semiordered structure, so-called Liesegang rings [6]. Periodic ring-shaped structures are clearly seen in Fig. 2c. The appearance of bands is caused by the pe-

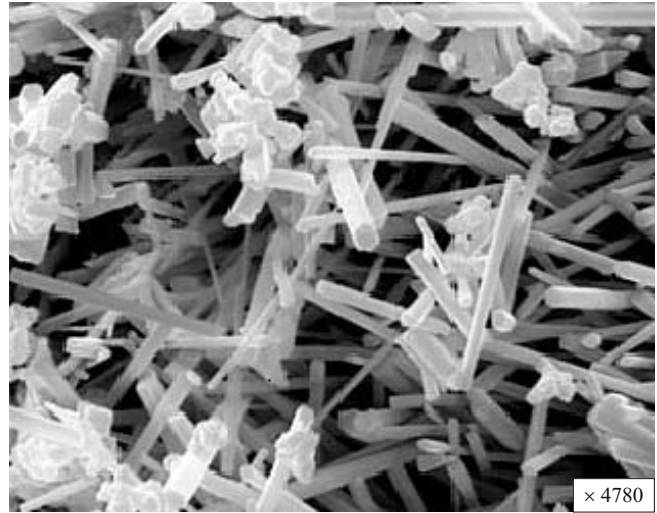


Fig. 1. Photomicrograph of the product of combustion of ferrosilicon in nitrogen.

riodicity of separation of particles of the solid phase formed, which is due to the fact that nuclei of the new phase are formed in rigorously defined supersaturation. Condensed silicon nitride is separated when the product of the activities of silicon and nitrogen in the melt is greater than $SP_{Si_3N_4}$ at the given temperature. As soon as the product of the activities becomes equal to $SP_{Si_3N_4}$, separation of silicon nitride stops.

The amount of nitrogen “leaving” the melt is compensated by gaseous nitrogen in accordance with the value of the solubility of nitrogen in the Fe – Si melt for the given temperature and pressure. When the amount of newly dissolved nitrogen again exceeds $SP_{Si_3N_4}$, the melt becomes supersaturated relative to N and Si and the next portion of silicon nitride is formed.

Some features of the microstructure of the combustion products hardened in initial nitration also indicate growth of crystals from the melt (Fig. 3). Hollows, which are probably the basal faces through which the crystallizable material reached the growing crystal, are visible on the surface of the solidified melt. Since crystallization does not take place uniformly due to the essentially nonisothermal conditions of SHS and due to mixing of the melt and evaporation of silicon, the crystallizable substance reached the growing crystal not in a continuous stream but in different amounts at certain times. For this reason, a crystal growing from the melt is distinguished by high defectiveness and does not have a normal face.

At the same time, many experimental data show that in addition to crystals with defects in the crystal structure, most crystals have a proper crystallographic face of both the sides and the apex (see Fig. 1). In addition to crystallization from the melt, silicon nitride crystals probably also grow through the gas phase. At synthesis temperatures above 1500°C, silicon evaporates from the eutectic melt and the equilibrium

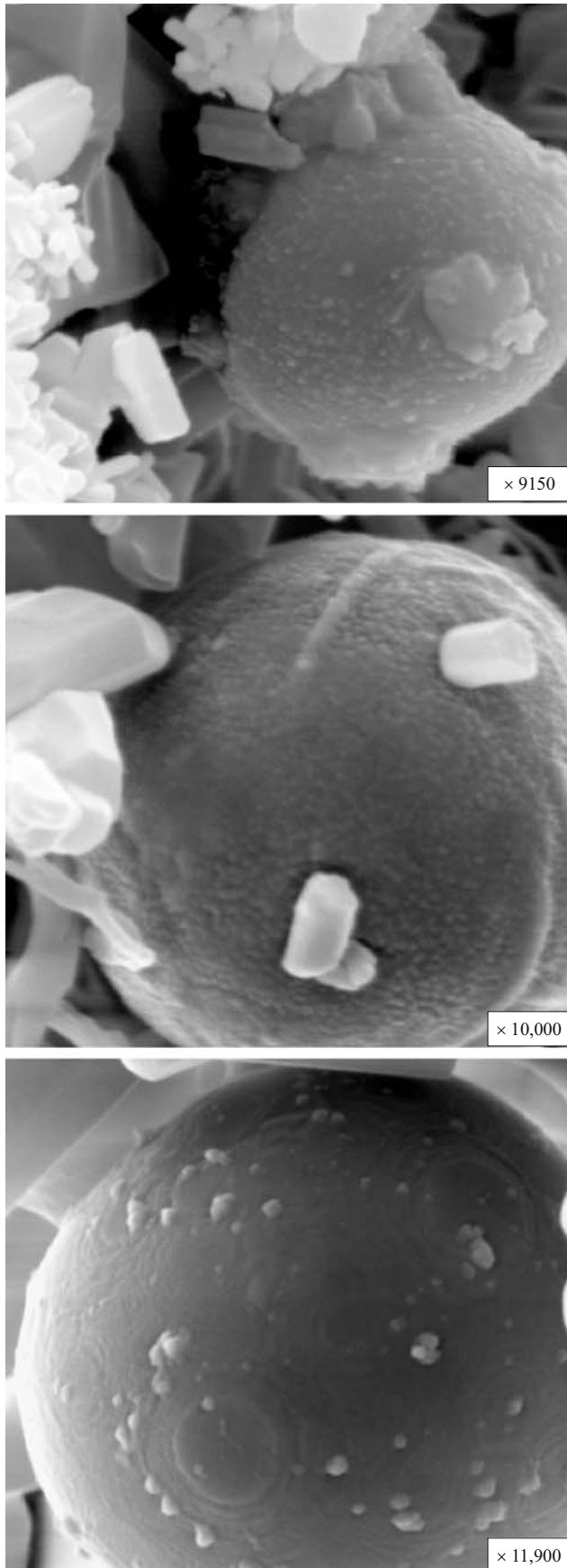


Fig. 2. Microstructure of iron – silicon alloys.

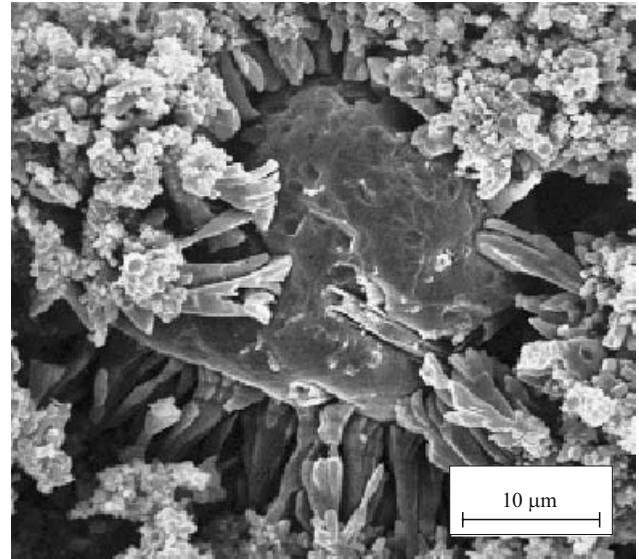


Fig. 3. Microstructure of a hardened sample in the initial stage of nitration.

silicon vapor pressure becomes significant [7]. In addition, silicon particles less than 10 μm in size pass into the gas phase during SHS due to evaporation [3].

The vapor – liquid – crystal (VLC) mechanism is one of the mechanisms of growth of crystals from the gas phase. A sufficient sign of crystal growth by the VLC mechanism is the presence a hemispherical particle — a globule — at the apex of the whisker. Characteristic globules were found in electron microscopic studies of combustion products (Fig. 4*a* and *b*). According to the VLC mechanism, conversion of whiskers into lamellar crystals formed by anisotropic growth of the side face of a whisker is possible as a function of the crystallization conditions (temperature, supersaturations, etc.). The microstructure of silicon nitride, whose crystals are lamellar in shape, is shown in Fig. 4*c*.

The experimental data on the features of structural formation in combustion of ferrosilicon in nitrogen thus show that silicon nitride crystals grow both by the VLC mechanism and through solution — crystallization from a melt. The ratio of the contributions of these mechanisms during structural formation of silicon nitride is determined by the conditions of synthesis. The mechanism of growth of silicon nitride crystals from a melt is characteristic of combustion of ferrosilicon in nitrogen, while in combustion of silicon in nitrogen, crystals only grow according to the VLC mechanism.

In conclusion, it is necessary to note that the presence of a melt in combustion of ferrosilicon in nitrogen causes further evolution of the structure, ensuring the conditions for collective recrystallization (secondary structural formation [8]). The size of the silicon nitride crystals increases during ripening when large crystals grow due to dissolution of small crystals, promoted by high temperature, the presence of a melt, and slow cooling of the sample.

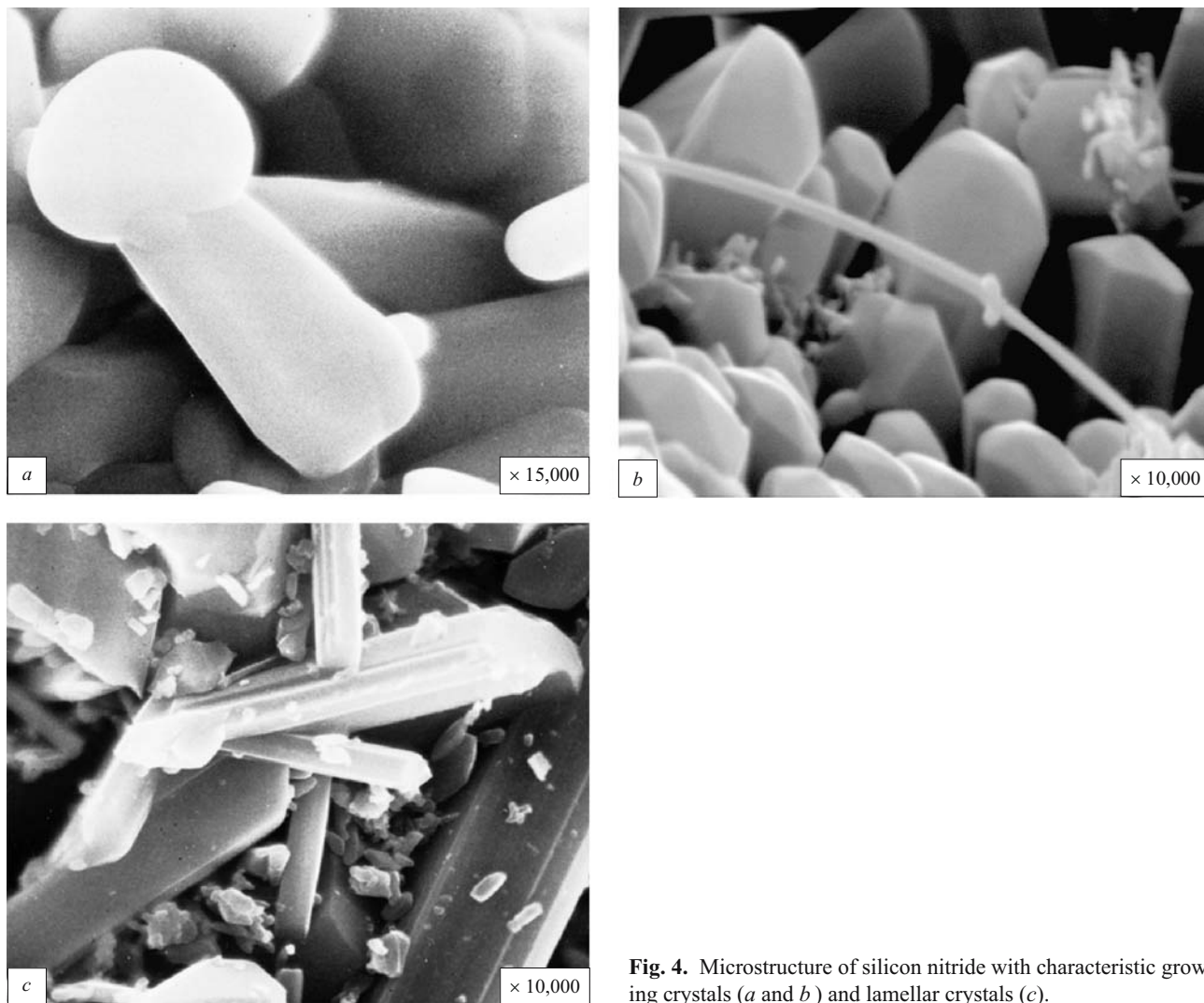


Fig. 4. Microstructure of silicon nitride with characteristic growing crystals (*a* and *b*) and lamellar crystals (*c*).

REFERENCES

1. R. A. Andrievskii and I. I. Spivak, *Silicon Nitride and Materials Made from It* [in Russian], Metallurgiya, Moscow (1984).
2. A. S. Mukas'yan, V. M. Martynenko, A. G. Merzhanov, et al., "Mechanism and characteristics of combustion of silicon in nitrogen," *Fiz. Goreniya Vzryva*, No. 5, 43 – 49 (1986).
3. A. S. Mukas'yan, B. V. Stepanov, Yu. A. Gal'chenko, and I. P. Borovinskaya, "Mechanism of structural formation of silicon nitride in combustion of silicon in nitrogen," *Fiz. Goreniya Vzryva*, No. 1, 45 – 52 (1990).
4. L. N. Chukhlomina, Yu. V. Ivanov, Yu. M. Maksimov, et al., "Obtaining submicron silicon nitride powders by self-propagating high-temperature synthesis," *Neorg. Mater.*, **41**(12), 1294 – 1300 (2005).
5. E. I. Givargizov, *Growth of Whiskers and Lamellar Crystals from Vapor* [in Russian], Nauka, Moscow (1977).
6. O. G. Kozlova, *Morphological and Genetic Analysis of Crystals* [in Russian], Izd. MGU, Moscow (1991).
7. A. J. Moulson, "Reaction-bonded silicon nitride: its formation and properties," *Mater. Sci.*, **14**(5), 1071 – 1052 (1979).
8. A. G. Merzhanov, *Combustion Processes and Materials Synthesis* [in Russian], Chernogolovka (1998).